Aug 2014 – Oct. 2014, Vol. 4, No. 4; 3131-3139. E- ISSN: 2249 –1929

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT Research Article

pH- Metric Study Studies of Transition Metal Complexes With Substituted Imidazolinone Drug In Mixed Solvent System at a Constant Ionic Strength.

R. R. Tayade[1], Alice. S. Chandami[2], M.P. Wadekar*

Applied Chemistry Division, Govt. Vidarbha Institute of Science and Humanities*, Amravati, Maharashtra, India-444604.

Received: 25 August 2014; **Revised:** 15 September 2014; **Accepted:** 10 October 2014

Abstract: The interaction between Ni(II), Cu(II) and Zn(II) metal ions and substituted imidazolinone have been studied at 0.1 M Ionic Strength in 70 % DMF-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Ni(II), Cu(II) and Zn(II) metal ions form 1:1 complex with ligands **(L1& L2).** The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (logk). From estimated data (pK and log k), the effects of substituents were studied. Ligand used for present work were **(L1)** 1-[2-hydroxy-5-(3 Chloro phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline **(L2)**1-[2-hydroxy-5-(4-bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline.

Keywords: 1-[2-hydroxy-5-(substituted phenylazo)benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline, 70% DMF-water mixture, proton-ligand stability Constants(pK), metal-ligand stability constant(logK).

INTRODUCTION

Literature survey reveals that compound bearing azo group exhibit various biological activity, imidazoline-5-(4H)-one exhibit promising biological and pharmacological activity. Interest in the

chemistry of imidazoline continuously increases because of their usefulness as antibacterial[1] and anti-inflammatory[2] agents. Some of them may be useful in the polymer chemistry. Moreover imidazoline and 5-oxo imidazoline have great therapeutic importance such as anticonvulsant, potent CNS depressant, sedative and hypnotics, hypotensive and potent antiparkinsonian activity[3] promoted by these observations. Imidazolinone ring system is of biological and chemical interest since long. The imidazolinones[4]are associated with therapeutic activities such as MAO inhibitory, antihelmintical and herbicidal activities. Some workers have recognized 5-imidazolone as having anticancer activity. The therapeutic importance of the compounds inspired us to synthesize some potential imidazolinones. M. P. Wadekar *et al*.[5] gives a method of synthesis of series of 1-(2-hydroxy-5-(substituted phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxo imidazolines carrying azo linkages. This gives importance to the study physicochemical properties of substituted imidazolinone.

The complexes have been extensively studied in solution as well as in solid state by many workers, due to it's remarkable properties and high stability. With the help of various experimental techniques, the extensive work in coordination complexes has been made possible and has lead in a number of empirical conclusions which have been detailed by Martell[6]. The stability of complex in solutions is depending on nature of central metal ion and ligands. The most important characteristics of the central atom which influence the stability of complex compounds are the degree of oxidation, the radius and electronic structure. Stability is dependent on the same characteristic in the ligand as considered for the cation in the case of complexes with monoatomic ligands. The strength of binding of ligand to the central metal ion is depending on structure of ligand molecule or ions[7- 8]. The stability of complexes is dependent upon the size and number of chelating rings also. The structure of chelating agent determines the size of the chelating rings and the number of rings formed on chelation. The stability order of metal complexes of transition metal ion was found by Irving and Williams[9]as Mn2+<Fe2+<Ni2+<Cu2+>Zn2+.Ayesha Durrani[10], Y. K. Meshram[11], D. M. Janrao[12], S. V. Thakur[13] studied the stability constant of transition metal complexes at a constant ionic strength in a mixed solvent medium. The thermodynamic physibility of metal interaction with ligand has investigated by Kaur[14], Syed Ahmad[15] and S. V. Thakur[16]. Charge on metal and ligand also affected on a stability of complexes. Kiranapure *et al*.[17], Wasu *et al*.[18] investigate the effect of dielectric constant on metal-ligand stability. Many worker study the stability constant of lanthanide metal having different charge in binery and tarnary solvent[19-20]

In the present work, effect of metal ions such as Ni(II), Cu(II) and Zn(II) on the properties of complexes of substituted imidazolinone in 70% DMF + water mixture at 298K had studied.

MATERIALS AND METHOD

Ligands (Substituted imidazolinone drugs):

(L_1) 1-[2-hydroxy-5-(3-chloro phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline

(L_2)1-[2-hydroxy-5-(4-bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline

The ligands **(L_1)** & **(L_2)** were synthesized in the laboratory by known literature method[5]. The purity of these compounds exceeds 99.5% and structures were confirmed by NMR, IR and melting points. The stock solutions of the ligand was prepared by dissolving required amount of ligand in a minimum volume of 70% (DMF + water) mixture subsequently diluted to final volume.

Metal ions (divalent metal ion in nitrates forms):

Ni(II), Cu(II) and Zn(II).

Stock solution: 1M KNO_3 solution, 0.1M HNO_3 solution, 0.1M NaOH and 0.01M Transition metal ions solution are prepared in double distilled water. 0.01 M ligand (L1 and L2) solution in 70% DMF –water mixture.All the chemical used in experimental work are AR grades.

Calvin –Bjerrum titration methods: All pH-metric titrations and pH-measurements were carried out with EQIP-TRONIC DIGITAL pH meter model EQ-610 (accuracy + 0.05 units) with a glass and calomel electrodes assembly. at 25±0.10c in 70% DMF-water mixture and at an inert atmosphere by bubbling nitrogen gas .

General procedure: Types of Titrations;

i) Free acid HNO_3 (0.01 M)

ii) Free acid HNO_3 (0.01 M) and ligand (20 x 10^{-4}M)

iii) Free acid HNO_3 (0.01 M) and ligand (20 x 10^{-4}) and metal ion (4 x 10^{-4}M) against standard 0.1N NaOH solution.

The ionic strength of all the solutions was maintained constant 1M by adding appropriate amount of KNO_3 solution. All the titrations were carried out in 70% DMF-water mixture and the reading were recorded for each 0.2 ml addition. The graphs of volume of alkali added (NaOH) against pH were plotted.

Detection Method: Titration curves are used to estimate the values of $\overline{n_A}$ (proton -ligand formation numbers) which are presented in **Table 1-10**. Formation curve are constructed between $\overline{n_A}$ values and pH. The pH values at 0.5 $\overline{n_A}$ values corresponds the pK values (proton-ligand dissociation constants) of respective ligand. Proton ligand dissociation constants (pK values) are evaluated and presented in Table (3), which are calculated by Half Integral and Point wise calculations method.

RESULT AND DISCUSSION

The ligands involved in the present work may be considered as a monobasic acid having only one dissociable H^+ ion from phenolic-OH group and it can therefore, be represented as HL. The dissociating equilibrium can be shown as.

$$HL \rightleftharpoons H^+ + L^-$$

By the law of mass action, we have,

$$k = \frac{[H^+][L^-]}{[HL]} \qquad \ldots\ldots\ldots (1)$$

Where, the quantities in bracket denote the activities of the species at equilibrium.

Calculation of Proton-Ligand Stability Constant ($\overline{n_A}$) : The plots between volumes of NaOH and pH (**Fig-1 to 2**)of the solutions were used to determine the proton ligand stability constant (representing the replacement of H^+ from functional group of ligand with respect to pH value) and evaluate the proton-ligand stability constants of the ligands. The horizontal difference (V2-V1) was measured accurately between the titration curves of acids and acids + ligands. It was used to calculate

the formation number $\overline{n}_A$ at various pH values and fixed ionic strength μ = 0.1M using Irving and Rossotti's equation.[21-22]

$$\overline{n}_A = \gamma - \frac{(V_2 - V_1)(N + E^0)}{(V^0 + V_1)T_L^0} \quad \ldots\ldots\ldots (2)$$

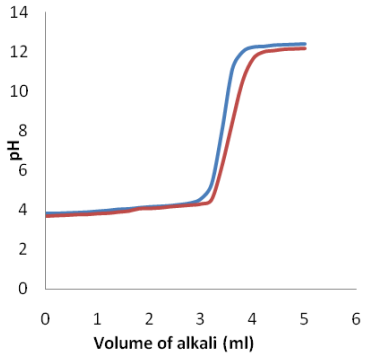

Fig. 1: pH metrix titration free +L_1

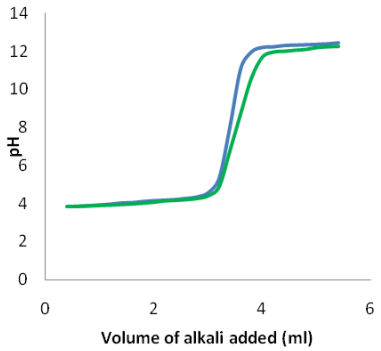

Fig. 2: pH metrix Free titration acid +L_2

Where, V_0 is the initial volume of the solution. E_0 and TL_0 are initial concentrations of the mineral acid and ligand respectively. V_1 and V_2 are the volumes of alkali of normality N during the acid and ligand titration at given pH. γ is the replaceable proton from the ligand.

The data of $\overline{n}_A$ values obtained at various pH along with the horizontal difference for some representative systems are presented in **Table 1 to 2**. (**fig 3 to 4**)

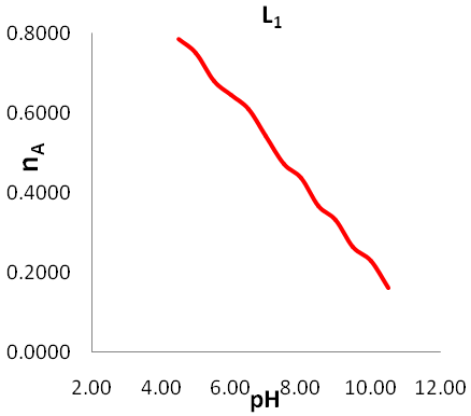

Fig.3 : Formation Curve of $\overline{n}_A$ Vs pH

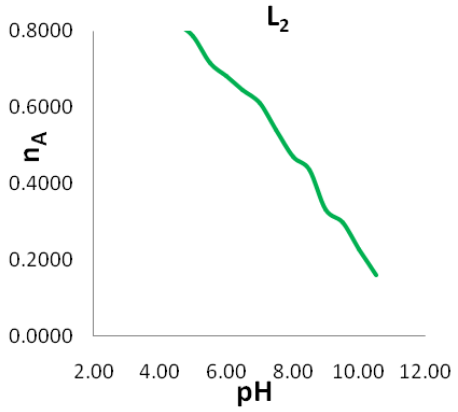

Fig.4 : Formation Curve of $\overline{n}_A$ Vs pH

Table –1: Determination of $\overline{n_A}$ Values of L_1

pH	V1	V2	V2-V1	$\overline{n_A}$
4.50	3.00	3.06	0.06	0.7857
5.00	3.15	3.22	0.07	0.7513
5.50	3.21	3.30	0.09	0.6810
6.00	3.25	3.35	0.10	0.6460
6.50	3.28	3.39	0.11	0.6110
7.00	3.33	3.46	0.13	0.5411
7.50	3.36	3.51	0.15	0.4711
8.00	3.40	3.56	0.16	0.4366
8.50	3.43	3.61	0.18	0.3669
9.00	3.46	3.65	0.19	0.3324
9.50	3.49	3.70	0.21	0.2629
10.00	3.53	3.75	0.22	0.2289
10.50	3.56	3.80	0.24	0.1597
11.00	3.59	3.85	0.26	0.06
11.50	3.65	3.93	0.28	0.0227

Table – 2 : Determination of $\overline{n_A}$ Values of L_2

pH	V1	V2	V2-V1	$\overline{n_A}$
4.50	3.00	3.05	0.05	0.8214
5.00	3.15	3.21	0.06	0.7869
5.50	3.21	3.29	0.08	0.7164
6.00	3.25	3.34	0.	0.6814
6.50	3.28	3.38	0.10	0.6464
7.00	3.33	3.44	0.11	0.6117
7.50	3.36	3.49	0.13	0.5416
8.00	3.40	3.55	0.15	0.4718
8.50	3.43	3.59	0.16	0.4372
9.00	3.46	3.65	0.19	0.3324
9.50	3.49	3.69	0.20	0.2980
10.00	3.53	3.75	0.22	0.2289
10.50	3.56	3.80	0.24	0.1597
11.00	3.59	3.85	0.26	0.06
11.50	3.65	3.93	0.28	0.0227

Calculation of Proton-Ligand Stability Constant (logK) : The metal–ligand formation constant ($\overline{n}$) is estimated by Irving-Rossotti's equation.

$$\overline{n} = \frac{(V_3 - V_2)(N + E^0)}{(V^0 + V_2)\, n_A\, T_M{}^0} \qquad \text{..... (3)}$$

Where the notations have the same meaning as given in earlier equation in.The horizontal difference (V3-V2) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of $\overline{n}$ using Irving Rossotti's equation.

Table 3: Proton –Ligand stability Constants (pk values)

Ligand	pK (Half Integral Method)	pK (Pointwise Method)
(L_1)1-[2-hydroxy-5-(3-chlorophenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline	7.20	7.27
(L_2) 1-[2-hydroxy-5-(4-bromo phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline	7.50	7.54

pK ligand (L_2). > pK ligand (L_1).

Table – 4:
Determination of $\bar{n}$
System L_1 + Ni(II)

pH	V_2	V_3	V_3-V_2	$\bar{n}$
4.50	3.06	3.07	0.01	0.226
5.00	3.22	3.24	0.02	0.471
5.50	3.30	3.33	0.03	0.778
6.00	3.35	3.39	0.04	1.200
6.50	3.39	3.43	0.04	1.152
7.00	3.46	3.51	0.05	1.623
7.50	3.51	3.57	0.06	2.233

Table – 5:
Determination of $\bar{n}$
System L_1 + Cu(II)

pH	V_2	V_3	V_3-V_2	$\bar{n}$
4.50	3.06	3.07	0.01	0.226
5.00	3.22	3.25	0.03	0.707
5.50	3.30	3.34	0.04	1.037
6.00	3.35	3.40	0.05	1.365
6.50	3.39	3.45	0.06	1.729
7.00	3.46	3.53	0.07	2.272
7.50	3.51	3.59	0.08	2.978

Table – 6:
Determination of $\bar{n}$
System L_1 + Zn(II)

pH	V_2	V_3	V_3-V_2	$\bar{n}$
4.50	3.06	3.07	0.01	0.226
5.00	3.22	3.24	0.02	0.471
5.50	3.30	3.33	0.03	0.778
6.00	3.35	3.38	0.03	0.819
6.50	3.39	3.43	0.04	1.152
7.00	3.46	3.50	0.04	1.298
7.50	3.51	3.55	0.04	1.489

Table – 7:
Determination of $\bar{n}$
System L_2 + Ni(II)

pH	V_2	V_3	V_3-V_2	$\bar{n}$
4.50	3.05	3.07	0.02	0.434
5.00	3.21	3.24	0.03	0.675
5.50	3.29	3.33	0.04	0.986
6.00	3.34	3.39	0.05	1.294
6.50	3.38	3.44	0.06	1.635
7.00	3.44	3.51	0.07	2.011
7.50	3.49	3.57	0.08	2.592

Table – 8:
Determination of $\bar{n}$
System L_2 + Cu(II)

pH	V_2	V_3	V_3-V_2	$\bar{n}$
4.50	3.05	3.06	0.01	0.217
5.00	3.21	3.23	0.02	0.450
5.50	3.29	3.31	0.02	0.493
6.00	3.34	3.37	0.03	0.776
6.50	3.38	3.41	0.03	0.817
7.00	3.44	3.48	0.04	1.149
7.50	3.49	3.53	0.04	1.296

Table –9:
Determination of $\bar{n}$
System L_2 + Zn(II)

pH	V_2	V_3	V_3-V_2	$\bar{n}$
4.50	3.05	3.06	0.01	0.217
5.00	3.21	3.23	0.02	0.450
5.50	3.29	3.32	0.03	0.740
6.00	3.34	3.37	0.03	0.776
6.50	3.38	3.42	0.04	1.020
7.00	3.44	3.48	0.04	1.149
7.50	3.49	3.54	0.05	1.620

Table 10: Metal –Ligand stability Constants (LogK values)

System : Ligand	+ Metal	$\log K_1$	$\log K_2$	$\log K_1/\log K_2$	$\log k_1$-$\log k_2$
L_1	Ni(II)	4.94	4.05	1.21	0.89
	Cu(II)	5.14	2.55	2.01	2.59
	Zn(II)	4.84	2.95	1.64	1.89
L_2	Ni(II)	5.19	3.65	1.42	1.54
	Cu(II)	5.54	4.05	1.36	1.49
	Zn(II)	4.94	2.55	1.93	2.39

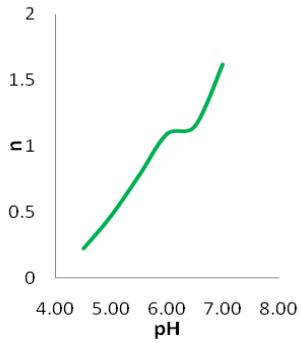

Fig. 5 : Plot of n Vs pH of Sysem-L_2 Ni(II)

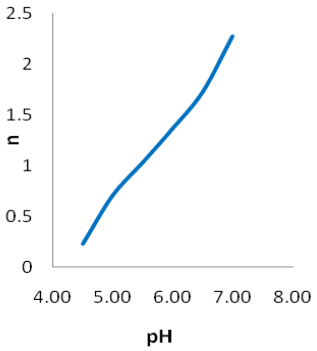

Fig. 6 : Plot of n Vs pH of Sysem-L_1 Cu(II)

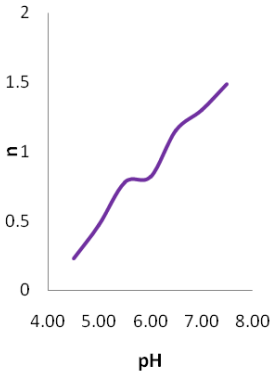

Fig. 7 : Plot of n Vs pH of Sysem-L_2 Zi(II)

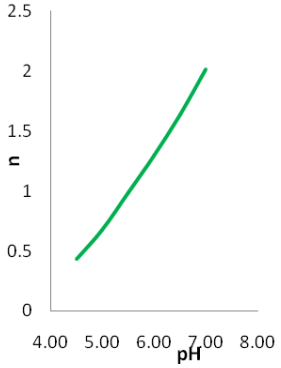

Fig. 8 : Plot of n Vs pH of Sysem-L_2 Ni(II)

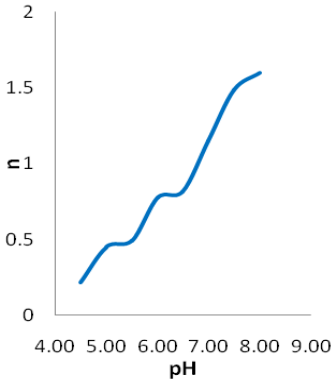

Fig. 9 : Plot of n Vs pH of Sysem-L_2 Cu(II)

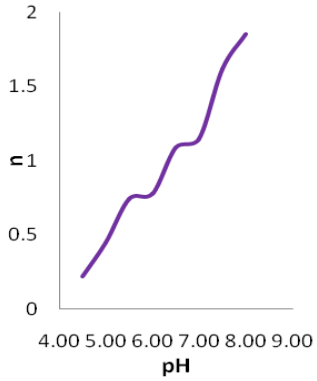

Fig. 10 : Plot of n Vs pH of Sysem-L_2 Zn(II)

pK value for both the ligand is small because substituent group present on a structure of ligand both are ring deactivating or electron withdrawing. But ligand L_2 has comparatively greater value than ligand L_1. Substituent at ligand L_1 is -3-Chroro and at ligand L_2 is -4-bromo, and it is known that chloro group is more deactivating than Bromo group. Hence the increment in pK value of ligand (L_2) is attributed to presence of less electron withdrawing group which decrease the activity of ligand L_2 in less amount thanL_1 to form more stable complex.

From the **table-10** it is observed that small difference between log K1 and logK2 values not more than 2.5 indicates the simultaneous formation of complex between metal ion and ligand.

If the ratio between metal- ligand stability constant ($logK_1$/ $LogK_2$) is greater than 1.5 then in such case there is a stepwise formation of metal ligand complex. From the table-j it is observed that, in case of Ni(II) ion there is a simultaneous formation of complex with both the ligand L_1 and L_2 and in case of Cu(II) and Zn(II) ion there is a stepwise formation of complex with both the ligand L_1 and L_2.

CONCLUSSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid +ligand + metal) curve for all systems started from pH = 3.90 this indicated the commencement of complex formation. Also change in colour from yellow to brown in the pH range from 3.90 to 11 during titration showed the complex formation between metal and ligand. The order of pK values of ligands is found to be as (Table-3).

ACKNOWLEDGEMENT

The author is very thankful to the Miss. Monali M. Kalskar, Govt. Vidarbha Institute of Science and Humanities, Amravati, state Maharashtra for kindly cooperation during research work.

REFERENCES

1. A.M.Dave, K.N.Bhatt , *J. Indian Chem. Soc*,1987, 64,348-353.
2. S.M.Sethna and R.C.Shah; *J. Indian Chem. Soc*., 1993, 1459.
3. P.Kumar, C.Nath and K Shankar*, Pharmazia*, 1985, 40, 267-275,
4. Vogel's Textbook of Practical Organic Chemistry 1956, (Fifth Edition), 1155.
5. M P Wadekar, Arun R Raut. *Der pharma chemical*, 2010, 2(1): 76-82.
6. A. E. Martell and M.Calvin "*Chemistry of metal chelate compound, Prentice Hall INC., England, Cliffs N.J., 1962,* 1502.
7. J.K. March*, J. Chem. Soc.,* 1951, 1461, 3057-3062.
8. Y.Shiokawa, R. Amano, *J. Radioanal. Nuc. Chem.,* 1991, 152 (2):373-378.
9. Irving H and Williams R J P, *J Chem Soc*, 1953, 3192.
10. Ayesha Durrani, *J.Chem. Bio. Phy. Sci. SecA*, 2014, 4(2), 927-930
11. Y. K. Meshram, R. F. Khan, *Ind.J.Appli.Res*, 2014, 4(3), 37-41.
12. D. M. Janrao, Jamil Pathan, *Sci.Revs.Chem.Commun*, 2014, 4(1), 11-24.
13. S. V. Thakur, M. Farooqui, *J.Chem.Bio.Phy.Sci.SecA*, 2014, 4(1), 01-07.
14. H. Kaur, A. Singla, *Int.J.Theoro.Appli.Sci.*, 2010, 2(1), 14-17.
15. Syed Ahmad Tirmazi, M.H.Sarwar Wattoo, *Arabian J Sci.Engg*., 2009, 34(2A), 43-48.
16. S. V. Thakur, M. Farooqui,*Der Chemica Sinica*, 2012, 3(6),1406-1406.
17. K. T. Kiranapure, P. J. Sondawale, *Ori.J.Chem*, 2010, 26(2), 565-571.
18. M. B. Wasu, P. H. Bhagwat, *Int.J.Chem.Sci*. 2010, 8(2), 791-796.
19. S. D. Thakur, D.T. Mahajan, *Der Pharma Chemica*, 2011, 3(6), 165-173.

20. A. N. Sonar, Rasayan J. Chem., 2011, 4(2), 405-407.
21. M. Calvin and K.Wilson , *J. Am Chem Soc*,1945, 67,2003-2015.
22. H. Irving and H. Rossotti , *Acta Chem Scand*, 1956, 10,72-78.

***Corresponding author: R.R. Tayade;**
Applied Chemistry Division, Govt. Vidarbha Institute of Science and Humanities*,
Amravati, Maharashtra, India-444604.